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An ab initio SCF computational approach is used to study six azines (azabenzenes) and their mononitro derivatives. Our primary interest is in determining how the reactive properties of the azines are affected by the introduction of the nitro group. All structures are optimized at the 3-21G level, and these are then used to compute the STO-5G molecular electrostatic potentials. Among the various isomers those having two adjacent ring nitrogens are by far the least stable. The nitro derivatives are most stable when the substituent is β to a ring nitrogen and least when it is α. The dominant features of the electrostatic potentials of these

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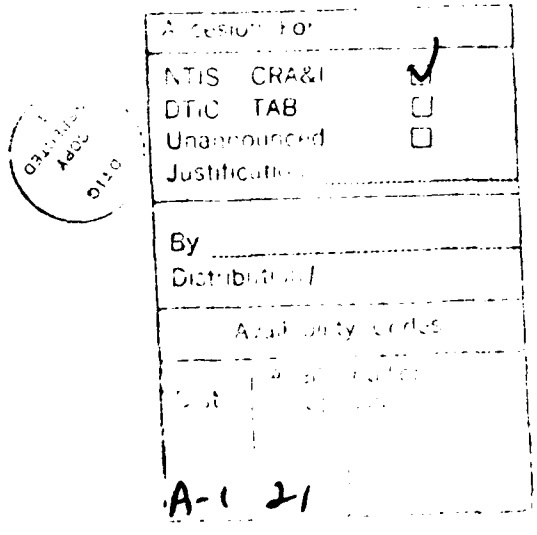

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A COMPUTATIONAL STUDY OF THE STRUCTURES AND ELECTROSTATIC POTENTIALS OF SOME AZINES AND NITROAZINES

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(Received 22 April 1988)

ABSTRACT

An ab initio SCF computational approach is used to study six azines (azabenzenes) and their mononitro derivatives. Our primary interest is in determining how the reactive properties of the azines are affected by the introduction of the nitro group. All structures are optimized at the 3-21G level, and these are then used to compute the STO-5G molecular electrostatic potentials. Among the various isomers, those having two adjacent ring nitrogens are by far the least stable. The nitro derivatives are most stable when the substituent is β to a ring nitrogen and least when it is α. The dominant features of the electrostatic potentials of these molecules are the large and strong negative regions, centered in the molecular planes, that are associated with the ring nitrogens and are indicative of their basic characters. These negative potentials, and correspondingly the basicities, become weaker as the number of ring nitrogens increases and also with the substitution of the electron-withdrawing nitro group. The regions above and below the rings become increasingly positive in going from the mono- to the tetra-azine and with the introduction of the $-NO_2$ group, suggesting enhanced susceptibility to nucleophilic attack.

INTRODUCTION

The azines, or azabenzenes, are an interesting class of molecules which can be regarded as related to benzene through the replacement of one or more carbons by nitrogens. The presence of the latter introduces a degree of basicity, but the electron-attracting tendencies of the nitrogens reduce the aromaticity of the ring and its reactivity toward electrophiles; indeed there develops a susceptibility toward nucleophilic attack [1].

Our primary interest in this work is in how these properties are affected by the introduction of the nitro group, which is very strongly electron-withdrawing, primarily through induction [2]. Accordingly a computational analysis of the azines **I–VI** and their mononitro derivatives **VII–XVII** has been carried out. For comparison, nitrobenzene, **XVIII** was also included. For all these molecules, structures and electrostatic potentials have been computed, the latter

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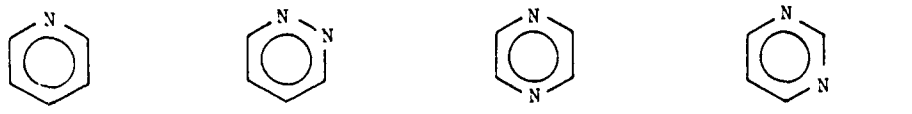
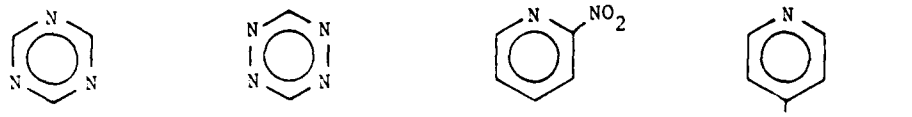
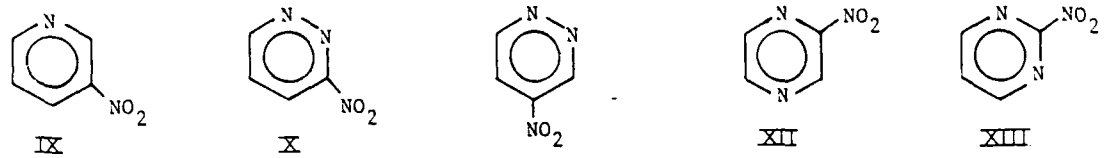
being well-established as a means for interpreting and predicting molecular reactive behaviour [3–5].



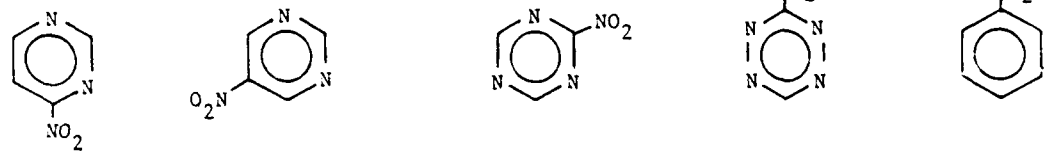
I, pyridine II, pyridazine III, pyrazine IV, pyrimidine



V, s-triazine VI, s-tetrazine VII VIII



IX X XI XII XIII



XIV XV XVI XVII XVIII

METHODS

An ab initio self-consistent-field molecular orbital procedure (GAUSSIAN 82 [6]) was used to determine the optimized structures of molecules **I–XVIII**. The optimizations were carried out at the 3-21G level, which has been shown to be effective for this purpose [7].

The electrostatic potential $V(\vec{r})$ that is created in the space around a molecule by its nuclei and electrons is expressed rigorously by eqn. (1)

$$V(\vec{r}) = \sum_{A} \frac{Z_A}{|\vec{R}_A - \vec{r}|} - \int \frac{\rho(\vec{r}')\mathrm{d}\vec{r}'}{|\vec{r}' - \vec{r}|} \qquad (1)$$

where Z_A is the charge on nucleus A, located at $\vec{R}_A$, and $\rho(\vec{r})$ is the electronic density function, computed from the molecular wave function.

The electrostatic potential has been demonstrated to be a useful tool for gaining insight into the reactive properties of molecules, especially toward electrophilic attack [3–5]. The first term on the right side of eqn. (1) is the positive contribution of the nuclei, while the second represents the negative effect of the electrons. Thus an approaching electrophile will tend initially to

go to those regions in which $V(\vec{r})$ is negative, and particularly to the points at which its most negative values (local minima) occur. It is important to note that the electrostatic potential is a real physical property, which can be determined experimentally as well as computationally [5].

$V(\vec{r})$ was calculated for molecules **I–XVIII** in terms of the STO-5G basis set, using the 3-21G optimized geometries. The former basis was found to be more reliable for properties related to the electronic charge distribution.

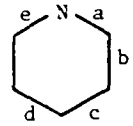
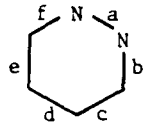
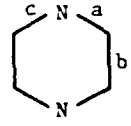
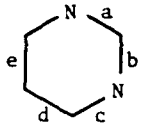
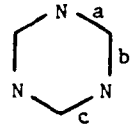
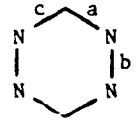
		Distances (A)	Angles (deg)
I		a: 1.331 (1.338) b: 1.383 (1.394) c: 1.384 (1.392)	e-a: 119 (116.9) a-b: 123 (123.8) b-c: 119 (118.5) c-d: 119 (118.4)
II		a: 1.355 (1.330) b: 1.316 (1.341) c: 1.395 (1.393) d: 1.365 (1.375)	f-a: 119 (119.3) b-c: 123 (123.7) c-d: 117 (117.1)
III		a: 1.331 (1.339) b: 1.381 (1.403)	c-a: 118 (115.6) a-b: 121 (122.2)
IV		a: 1.329 (1.340) c: 1.332 (1.340) d: 1.382 (1.393)	a-b: 125 (127.6) b-c: 118 (115.5) c-d: 122 (122.3) d-e: 117 (116.8)
V		a: 1.330 (1.319)	a-b: 124 (126.8) b-c: 116 (113.2)
VI		a: 1.329 (1.334) b: 1.332 (1.321)	c-a: 125 (127.4) a-b: 118 (116.0)

Fig. 1. Calculated structures of the unsubstituted azines **I–VI**. Experimentally determined values are in parentheses [1]. All the molecules are planar.

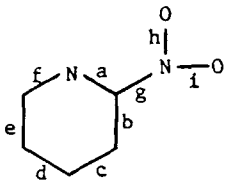
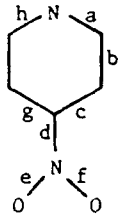
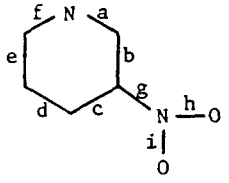
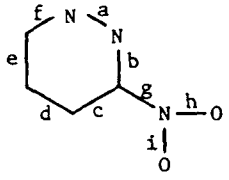
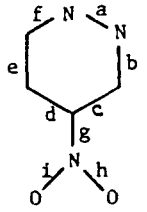
		Distances (A)		Angles (deg)	
VII		a: 1.305	f: 1.329	a-b: 124	f-a: 119
		b: 1.374	g: 1.460	b-c: 118	b-g: 119
		c: 1.383	h: 1.228	c-d: 119	h-i: 126
		d: 1.384	i: 1.253	d-e: 118	g-h: 118
		e: 1.385		e-f: 119	
VIII		a: 1.330		h-a: 119	
		b: 1.382		a-b: 122	
		c: 1.375		b-c: 117	
		d: 1.454		c-g: 121	
		e: 1.242		c-d: 119	
				e-f: 126	
IX		a: 1.326	f: 1.333	a-b: 121	f-a: 119
		b: 1.379	g: 1.440	b-c: 120	b-g: 120
		c: 1.378	h: 1.243	c-d: 118	g-h: 117
		d: 1.380	i: 1.244	d-e: 118	h-i: 125
		e: 1.383		e-f: 123	
X		a: 1.350	f: 1.319	a-b: 119	f-a: 119
		b: 1.294	g: 1.462	b-c: 125	b-g: 117
		c: 1.387	h: 1.226	c-d: 116	g-h: 118
		d: 1.364	i: 1.253	d-e: 118	h-i: 126
		e: 1.395		e-f: 123	
XI		a: 1.356	f: 1.315	a-b: 120	f-a: 120
		b: 1.314	g: 1.444	b-c: 122	c-g: 120
		c: 1.388	h: 1.241	c-d: 119	g-h: 117
		d: 1.357	i: 1.242	d-e: 116	h-i: 126
		e: 1.395		e-f: 123	

Fig. 2. Calculated structures of the nitroazines **VII-XI**. All the molecules are planar.

RESULTS AND DISCUSSION

Structures and stabilities

The key features of the 3-21G optimized structures of the azines and their

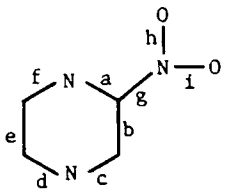
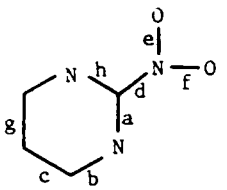
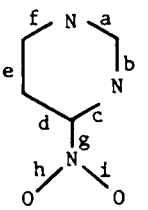
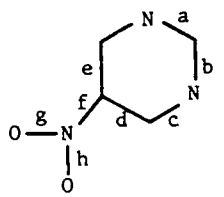
		Distances (A)		Angles (deg)	
XII		a: 1.306	f: 1.330	a-b: 123	f-a: 118
		b: 1.377	g: 1.452	b-c: 119	a-g: 117
		c: 1.329	h: 1.227	c-d: 119	g-h: 118
		d: 1.332	i: 1.252	d-e: 121	h-i: 126
		e: 1.382		e-f: 120	
XIII		a: 1.306		h-a: 127	
		b: 1.332		a-b: 117	
		c: 1.376		b-c: 121	
		d: 1.470		c-g: 118	
		e: 1.240		h-d: 117	
				e-f: 126	
XIV		a: 1.328	f: 1.333	a-b: 124	f-a: 118
		b: 1.330	g: 1.464	b-c: 118	c-g: 117
		c: 1.303	h: 1.251	c-d: 123	g-h: 116
		d: 1.372	i: 1.226	d-e: 115	h-i: 126
		e: 1.383		e-f: 122	
XV		a: 1.331		a-b: 125	
		b: 1.331		b-c: 118	
		c: 1.327		c-d: 120	
		d: 1.378		d-e: 119	
		f: 1.432		d-f: 121	
		g: 1.243		g-h: 126	

Fig. 3. Calculated structures of the nitroazines **XII**–**XV**. All the molecules are planar.

nitro derivatives are shown in Figs. 1–4. Their total energies and the relative energies within the various groups of isomers are listed in Table 1.

For the unsubstituted azines the experimentally determined structural data are available [1], and are also given in Fig. 1. Our calculated results are in generally good agreement with these, the largest differences being 0.025 Å and 2.8°. The C–C, C–N and N–N bond lengths are intermediate between their typical single- and double-bond values [8], consistent with these molecules having some degrees of aromatic character [1]; in particular, most of the C–C distances are very similar to that in benzene. With regard to the nitro derivatives, the principal structural effect of introducing the $-NO_2$ group is to shorten the bonds leading to the site of substitution.

	Distances (A)		Angles (deg)	
XVI	a: 1.308	f: 1.333	a-b: 126	f-a: 116
	b: 1.307	g: 1.469	b-c: 116	a-g: 117
	c: 1.334	h: 1.235	c-d: 123	h-i: 127
	d: 1.328		d-e: 117	
	e: 1.329		e-f: 123	
XVII	a: 1.312		f-a: 126	
	b: 1.329		a-b: 117	
	c: 1.312		b-c: 117	
	g: 1.459		c-d: 125	
	h: 1.235		f-g: 117	
			h-i: 127	
XVIII	a: 1.378		e-a: 122	
	b: 1.381		a-b: 119	
	c: 1.386		b-c: 120	
	f: 1.449		c-d: 120	
	g: 1.244		e-f: 119	
			g-h: 125	

Fig. 4. Calculated structures of the nitroazines **XVI** and **XVII**, and of nitrobenzene, **XVIII**. All the molecules are planar.

The relative stabilities of the various isomers show certain definite patterns (Table 1). It is clear that having two nitrogens adjacent to each other in the ring confers considerable instability upon the system; **II**, **X** and **XI** are all much less stable than their isomers. For the unsubstituted diazines **II–IV**, this has earlier been observed both experimentally [9] and computationally [10,11], and the same conclusions were reached in a recent study of the 1,4-dioxadiazines and their mononitro derivatives [12]. As before, we suggest that an important factor in this instability may be a tendency of these systems to decompose through the evolution of N_2.

Substitution of a nitro group does not change the order of stabilities of the diazines, which remains **II** < **III** < **IV**. However, certain preferences for the site of substitution can be discerned for both the nitropyridines and the nitrodiazines. The derivatives are most stable when the nitro group is on a carbon β to a ring nitrogen, and least when on the α carbon. This may reflect the electron-attracting tendency of the nitrogen, which depletes the electronic density around the α- and γ-positions (see structures **XIX–XXI**, for example) and makes them less favorable sites for the electrophilic nitro group. However, the effects of these site preferences upon the stabilities of the nitrodiazines are

TABLE 1

Calculated total and relative energies[a]

Molecule	Total energy, 3-21G (hartree)	Relative energies of isomers (kcal mol^{-1})[a]
I	−245.3120	
II	−261.1597	29.2
III	−261.1975	5.5
IV	−261.2062	0.0
V	−277.1011	
VI	−292.8894	
VII	−447.5980	1.8
VIII	−447.5982	1.7
IX	−447.6009	0.0
X	−463.4394	32.3
XI	−463.4414	31.1
XII	−463.4792	7.3
XIII	−463.4811	6.1
XIV	−463.4865	2.8
XV	−463.4909	0.0
XVI	−479.3703	
XVII	−495.1498	

[a]Within each of the three groups of isomers (**II–IV**, **VII–IX**, and **X–XV**), the relative energies are given in terms of the most stable isomer being assigned a value of zero.

much weaker than the striking destabilization due to two adjacent ring nitrogens (compare the energies of **X** and **XI** to those of **XII–XV** in Table 1).

XIX XX XIX XXI

Electrostatic potentials of unsubstituted azines

The electrostatic potentials of the unsubstituted azines, **I–VI**, have been presented and discussed previously [10] and, therefore, only certain key points will be mentioned here. The dominant features are the large and strong negative regions centered in the molecular plane, that are associated with the ring nitrogens and can be attributed to their lone pairs. (See Fig. 5, for example.) Due to the electron-withdrawing power of these nitrogens, nothing remains of the negative potentials that are found above and below the ring in benzene [13] (except to a small extent in the case of pyridine, **I**). These regions become increasingly positive in going from **I** to **VI**. This is consistent with observations

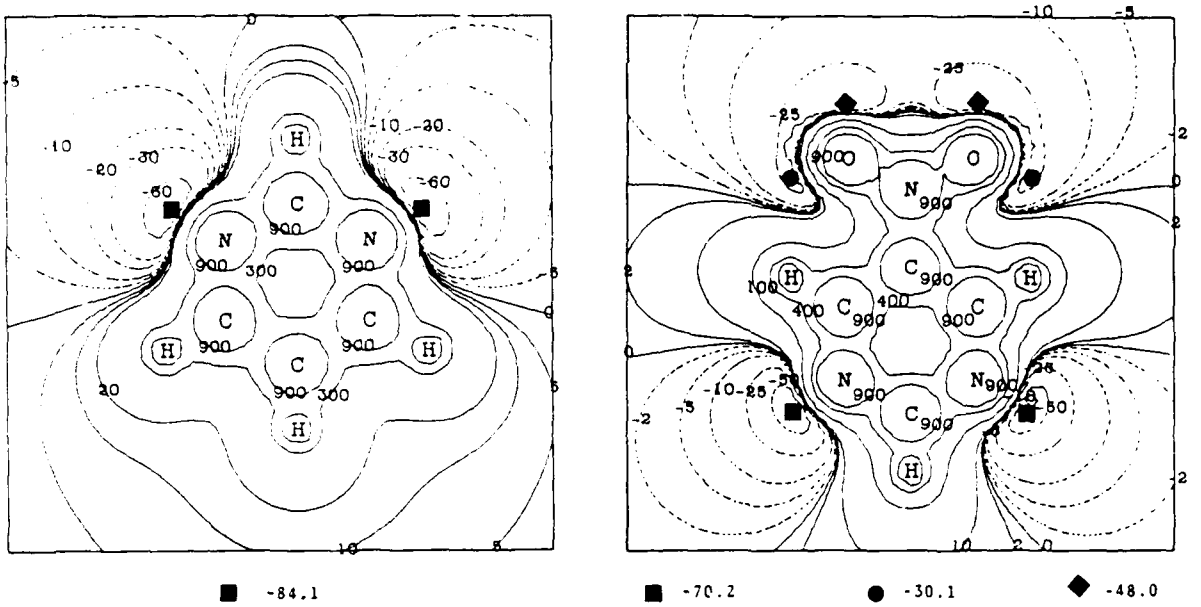


Fig. 5. Electrostatic potential (in kcal mol^{-1}) in the molecular plane of pyrimidine, **IV**. Dashed contours correspond to negative values. The positions of the most negative potentials are indicated, and the magnitudes are given below the figure.

Fig. 6. Electrostic potential (in kcal mol^{-1}) in the molecular plane of 5-nitropyrimidine, **XV**. Dashed contours correspond to negative values. The positions of the most negative potentials are indicated, and the magnitudes are given below the figure.

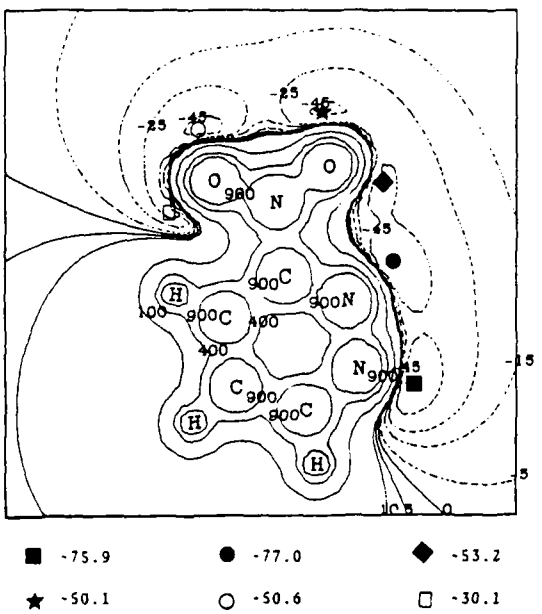


Fig. 7. Electrostatic potential (in kcal mol^{-1}) in the molecular plane of 3-nitropyridazine, **X**. Dashed contours correspond to negative values. The positions of the most negative potentials are indicated, and the magnitudes are given below the figure.

TABLE 2

Some properties of unsubstituted azines[a]

Molecule		Electrostatic potential minimum (kcal mol^{-1})	pK_a
	I	−92.9	5.2
	II	−90.1	2.1
	III	−84.1	1.1
	IV	−82.4	0.4
	V	−74.6	—
	VI	−67.3	—

[a]The electrostratic potential minima, all of which are asssociated with the ring nitrogens, were calculated in this work. The pK_a values are experimentally determined, and were taken from [1].

that the ring carbons are considerably less reactive toward electrophiles than in benzene, but more susceptible to nucleophilic attack [1]; both tendencies increase with the number of ring nitrogens.

The strongly negative electrostatic potentials produced by the ring nitrogens make these attractive sites for electrophiles, and indeed a variety of such reactions have been found to take place [1]. The magnitudes of these potentials decrease with the number of nitrogens in the ring, as shown in Table 2, reflecting the fact that as more nitrogens compete for the polarizable electronic charge, each receives a smaller share of it. This phenomenon has previously been noted in other systems containing electron-attracting atoms or groups [12,14–16]. Correspondingly, the reactivities toward electrophiles also decrease as the

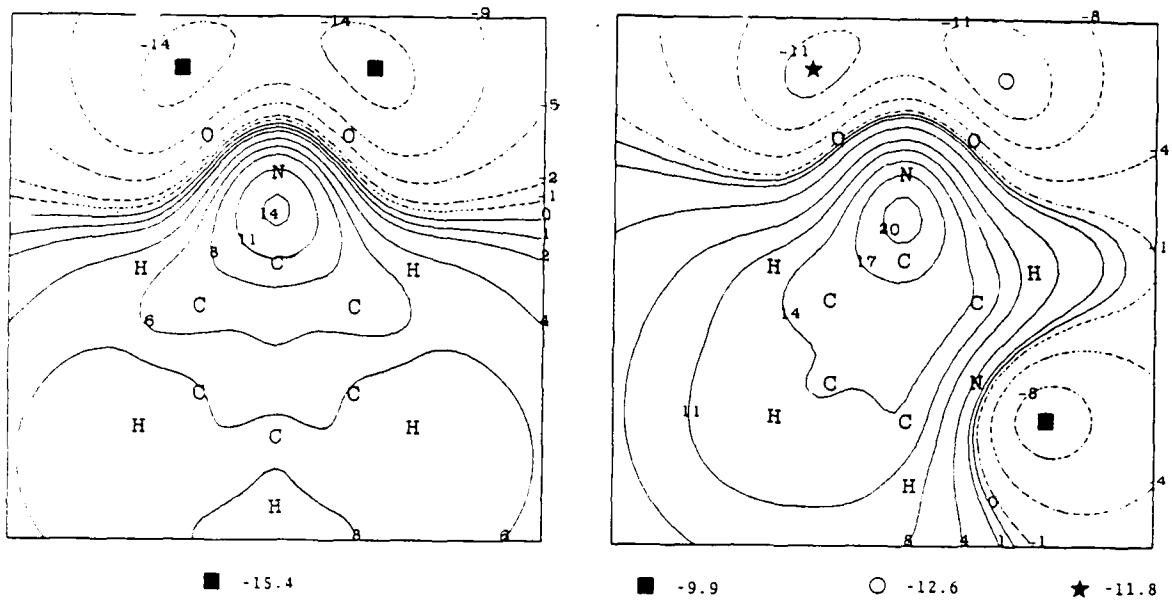


Fig. 8. Electrostatic potential (in kcal mol^{-1}) in the plane 1.75 Å above the molecular plane of nitrobenzene, **XVIII**. The projections of the nuclear positions are indicated. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are shown, and the magnitudes are given below the figure. The planar maximum, above the C-NO_2 bond region, is +14.4 kcal mol^{-1}.

Fig. 9. Electrostatic potential (in kcal mol^{-1}) in the plane 1.75 Å above the molecular plane of 3-nitropyridine, **IX**. The projections of the nuclear positions are indicated. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are shown, and the magnitudes are given below the figure. The planar maximum, above the C-NO_2 bond region, is +20.9 kcal mol^{-1}.

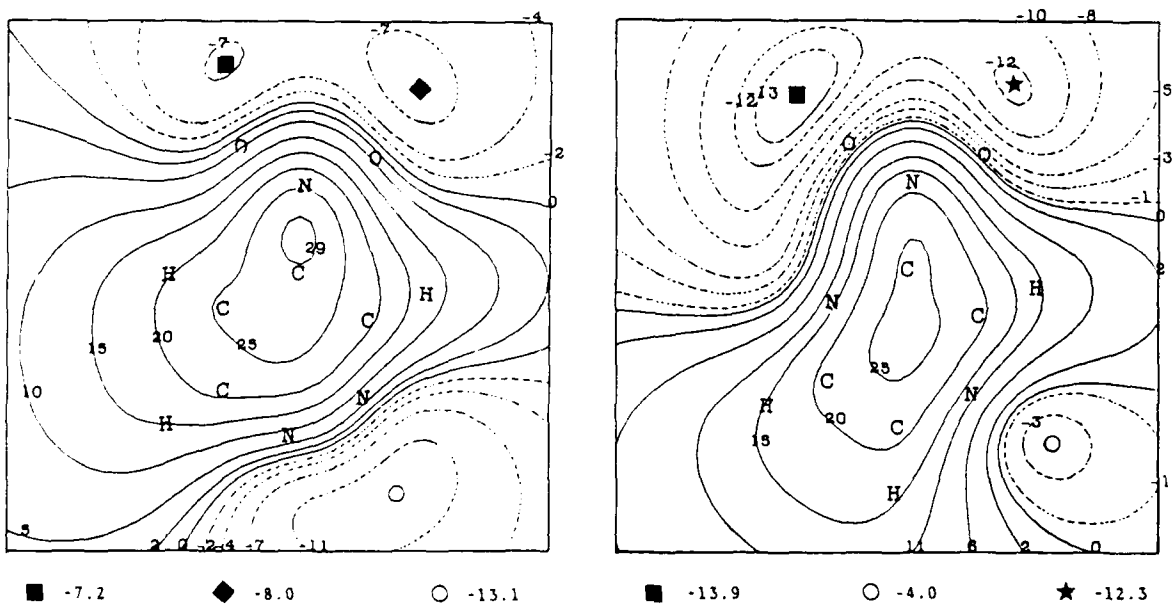


Fig. 10. Electrostatic potential (in kcal mol^{-1}) in the plane 1.75 Å above the molecular plane of 4-nitropyridazine, **XI**. The projections of the nuclear positions are indicated. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are shown, and the magnitudes are given below the figure. The planar maximum, above the C-NO_2 bond region, is +29.8 kcal mol^{-1}.

Fig. 11. Electrostatic potential (in kcal mol^{-1}) in the plane 1.75 Å above the molecular plane of 2-nitropyrazine, **XII**. The projections of the nuclear positions are indicated. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are shown, and the magnitudes are given below the Figure.

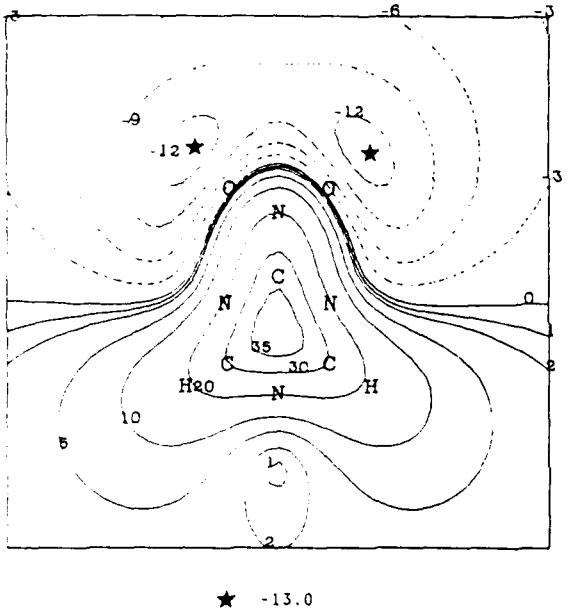
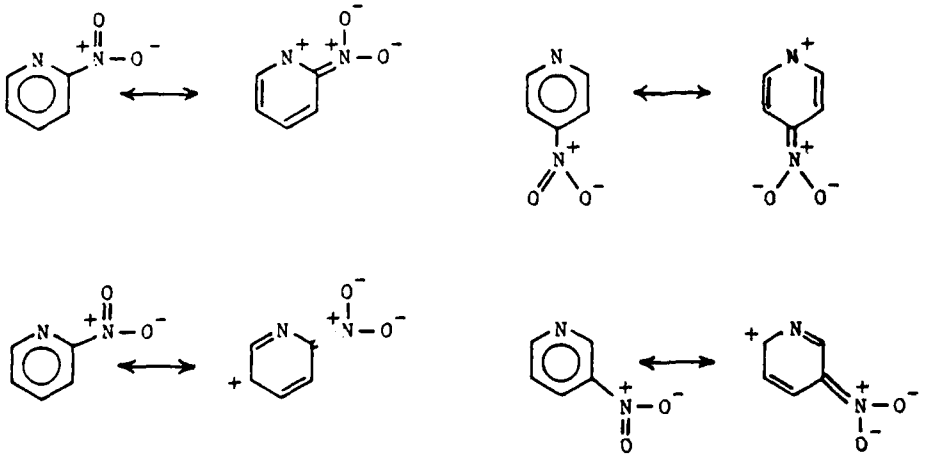


Fig. 12. Electrostatic potential (in kcal mol^{-1}) in the plane 1.75 Å above the molecular plane of nitro-*s*-triazine, **XVI**. The projections of the nuclear positions are indicated. Dashed contours correspond to negative values. The locations of the most negative potentials in this plane are shown, and the magnitudes are given below the Figure.

number of ring nitrogens increases [1]; for example, the basicities follow exactly the same trend as the potential minima, as seen from the pK_a values in Table 2. The experimentally observed proton affinities of pyridine and the three diazines also decrease in this order; thus the observed trend in this property can be explained without invoking hydrogen bonding in the protonated form, as was done earlier [11].

Electrostatic potentials of nitroazines

The substitution of a nitro group on an azine ring introduces another strong competitor for the polarizable electronic charge. Electron withdrawal by $-NO_2$ is primarily through induction [2], although a minor degree of conjugation does take place [17], as represented below for the nitropyridines.



It is to be anticipated, therefore, that the ring nitrogens will be less negative than in the unsubstituted azines, and similarly that the $-NO_2$ group will be less negative than in nitrobenzene, **XVIII**. Both of these expectations are borne out by our calculated electrostatic potentials.

The negative lone-pair potentials of the ring nitrogens are significantly weakened in going from the azines to their mononitro derivatives. This can be seen, for instance, by comparing Figs. 5 and 6; the values of the minima change from 84.1 kcal mol^{-1} in pyrimidine, **IV**, to -70.2 kcal mol^{-1} in 5-nitropyrimidine, **XV**. The latter value is fairly typical for the nitrodiazines, except when there is an overlapping and reinforcement of adjacent negative regions, as in **X** (Fig. 3), **XI** and **XIII**. For the nitropyridines, **VII–IX**, the minima are stronger, approximately -79 kcal mol^{-1} (compared to -92.9 in pyridine), while for **XVI** and **XVII** they range from -53.5 to -63.8 kcal mol^{-1}. Thus nitration should be accompanied by a general decrease in the basicities of the azines, as has indeed been observed for the nitropyridines [1].

The nitro groups in **VII–XVIII** have their customary extended regions of negative electrostatic potential near the oxygens [12,13,16,17]. These have four minima (Figs. 6 and 7), which can be interpreted as reflecting the oxygen lone pairs. The magnitudes of these minima in nitrobenzene, **XVIII**, are -41, -60, -60 and -41 kcal mol^{-1}; however, the presence of ring nitrogens weakens these to -35, -51, -51 and -35 kcal mol^{-1} in 4-nitropyridine, **VIII**, for example, and even further to -30, -48, -48 and -30 kcal mol^{-1} in 5-nitropyrimidine, **XV** (Fig. 6). Exceptions to these trends do of course appear when there is overlap of negative regions, as in **X** (Fig. 7).

The electrostatic potentials of all the nitro derivatives, **VII–XVIII**, are positive everywhere above and below the ring. This is true of nitroaromatics even when there are no nitrogens in the ring [13,17]. These positive regions are stronger for the nitroazines, however, as can be seen by comparing Figs. 8 and 9, and the difference becomes even more marked as the number of ring nitrogens increases (Figs. 10 and 11). Thus, while nitroazines should not undergo ring interactions with electrophiles, susceptibility toward nucleophilic attack is certainly to be anticipated.

In all the nitroazines these positive potentials tend to concentrate above the central regions of the rings, increasingly so for nitro-*s*-triazine and nitro-*s*-tetrazine (Figs. 9–12). However, in the nitropyridines, **VII–IX**, and in two of the nitrodiazines, **XI** and **XV**, the strongest build-up of positive potential in this plane occurs above the $C-NO_2$ bond region (see Figs. 9–11). This feature was previously observed in the nitro derivatives of a variety of unsaturated systems, including aromatics [13,17–19], dioxins [20], dioxazines and dioxadiazines [12], acetylene [16] and ethylene [21]. (This can be seen in Fig. 8 for the case of nitrobenzene.) We have shown that these positive build-ups can act as initial sites for nucleophilic attack, as in hydrolysis [18]. The magnitudes of build-up depends very much upon the remainder of the system. Thus

the electron-attracting effect of one ring nitrogen in **IX** causes this planar maximum to increase from 14 kcal mol^{-1} in nitrobenzene, **XVIII**, (Fig. 8) to 21 kcal mol^{-1} (Fig. 9), while the second ring nitrogen in **XI** produces a further increase to 30 kcal mol^{-1} (Fig. 10). Even more positive build-up was seen in dinitro derivatives, reaching 35 kcal mol^{-1} in dinitroacetylene [16] and approximately 50 kcal mol^{-1} in the dinitro-1,4-dioxadiazines [12].

SUMMARY

Our primary focus in this paper has been upon the relative stabilities and the electrostatic potentials of mononitroazines. We found that the preferred site for $-NO_2$ substitution is on a carbon β to a ring nitrogen, while the α position is the least stable. For both the unsubstituted diazines and their nitro derivatives, however, the most important destabilizing factor is the presence of two adjacent ring nitrogens.

The introduction of the strongly electron-withdrawing nitro group weakens the negative electrostatic potentials associated with the ring nitrogens, which should accordingly be significantly less basic than in the corresponding unsubstituted azines. (In the latter, the observed basicities follow the same trend as the magnitudes of the negative potentials near the ring nitrogens.) None of the nitroazines has any negative regions above or below the ring; instead there are positive build-ups above the central portions of the rings and sometimes above the $C-NO_2$ bonds, which are expected to provide channels for nucleophilic attack.

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